Plant. Skimmia wallichii Hk [13]; Rutaceae. *Occurrence.* A small procumbent shrub about 4 ft. high, fairly common in Singalila Range, from 9000–11 000 ft. *Previous work.* None. *Isolation and identification.* The powdered bark of the plant was extracted with C_6H_6 and the neutral fraction on chromatography over deactivated alumina first gave four crystalline compounds; the first mp 238–239°, $[\alpha]_D$ + 11°, ν_{max} 1710 cm^{-1} (six membered ring ketone) was identical with *taraxerone* (mmp and IR); 3-*epitaraxerol* [14] mp 261–263°, $[\alpha]_D$ −25·6°, ν_{max} 3420 cm^{-1} (–OH) and 825 cm^1 (trisubstituted double bond), acetate, mp 160–162°, $[\alpha]_D$ − 43. Oxidation of the alcohol by CrO_3–C_6H_5N complex-furnished taraxerone. The alcohol, 3-epitaraxerol and its oxidised product, taraxerone were identified by mmp, IR and co-TLC; *taraxerol*, mp 272–274°, $[\alpha]_D$ +5·5°, acetate, mp 295–297°, $[\alpha]_D$ +10° confirmed by mmp, IR and co-TLC with an authentic sample; and *sitosterol* (mmp and IR).

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BREVIFOLIN, CORILAGIN AND OTHER PHENOLS FROM *GERANIUM THUNBERGII*

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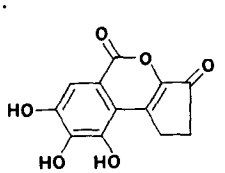
Key Word Index—*Geranium thunbergii*; Geraniaceae; polyphenols; brevifolin; corilagin; ellagic acid.

Plant. Geranium thunbergii Sieb. et Zucc. *Source.* Collected at Okayama University, August 1973. *Uses.* Official antidiarrhoics in Japan. *Previous work.* Isolation of gallic acid, succinic acid, quercetin [1], kaempferol-7-rhamnoside and kaempferitrin [2].



(1)

Present work. The aqueous extract of the aerial parts of the plant was concentrated and the ppt which formed was recrystallized from C_6H_5N to yield ellagic acid (IR). The mother liquor was concentrated to a syrup which was extracted with MeOH. The MeOH soln, on concentration gave solid KCl, and the filtrate (A) was then continuously extracted with Et_2O. The Et_2O extract gave a solid, recrystallized from MeOH, to give brevifolin **1**, $C_{12}H_{18}O_6$, (M^+ 248), m.p. >360°, trimethyl ether **2** (CH_2N_2), $C_{15}H_{24}O_6$, (M^+ 290), mp 209–210°. These data together with UV, IR,

NMR and MS spectra and comparison with authentic samples indicated **1** was brevifolin [3].

The mother liquor of **1** was concentrated to give succinic acid, the filtrate from which was diluted with Et_2O, and washed with 3% Na_2CO_3. Upon evaporation of Et_2O, a syrup was obtained and chromatographed over silicic acid, eluting with EtOAc, to give pyrogallol. The Na_2CO_3 washings were acidified (HCl), and extracted with Et_2O to give gallic acid. Both constituents were identified with authentic specimens by IR and mmp.

The aqueous layer (A) was extracted continuously with EtOAc. Evaporation of the EtOAc yielded an amorphous mixture which was positive to the colour tests of both ellagitannin ($NaNO_2$–AcOH) [4] and flavonoid (Mg–HCl). This mixture was: (i) acetylated and chromatographed over silicic acid to yield a crystalline acetate, $C_{49}H_{44}O_{29}$, mp 204°, $[\alpha]_D^{20}$ −24·5° ($CHCl_3$); (ii) methylated (CH_2N_2) and chromatographed over silicic acid to give a crystalline methyl ether, $C_{36}H_{40}O_{18}$, mp 228° (dec.), $[\alpha]_D^{16}$ −159·6° (Me_2CO). These data are identical with those of undeca-acetylcorilagin and nonamethylcorilagin, and the latter was identified by IR and mmp with the methyl ether from authentic corilagin.

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BIFLAVONOIDS AND XANTHONES OF *GARCINIA TERPNOPHYLLA* AND *G. ECHINOCARPA**

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Key Word Index—*Garcinia echinocarpa*; *G. terpnophylla*; Guttiferae; biflavonoids; xanthones; sitosterol.

A number of species of the genus *Garcinia* (Guttiferae) have already been examined for their constituents. We now report the isolation of five biflavonoids, four xanthones and sitosterol from *Garcinia echinocarpa* Thw. (Sinhala-Madol) and *Garcinia terpnophylla* Thw. (Sinhala-Kokatiya). Both plants are found in the wet forest of Sri Lanka and the latter is endemic to Sri Lanka. They were obtained from Kanneliya forest in South Sri Lanka. The timber is used for building purposes. The oil obtained from the seeds *Garcinia echinocarpa* Thw. is used for lighting lamps.

The timber and bark of the plants were separated, dried at 60°, powdered and extracted successively with light petroleum, C_6H_6 and MeOH. The MeOH extracts were further extracted with Et_2O. The compounds were isolated from the extracts by partitioning in a counter current apparatus, by preparative TLC and by column chromatography on silica gel or polyamide.

The following compounds were isolated and identified: *1,5-dihydroxyxanthone* mp 268–270° (acetone) lit. mp 268–270 [1] direct comparison and Co-TLC with authentic sample; *1,7-dihydroxyxanthone* (euxanthone), bright yellow needles mp 238–239° lit. mp 238–240° (acetone) [2] λ_{max}

* Part 18 in the series *Chemical Investigation of Ceylonese Plants.*